JOURNAL OF CATALYSIS 39, 286-293 (1975)

The Physicochemical Properties of the Bismuth Iron Molybdate System[1]

THOMAS NOTERMANN[2] AND GEORGE W. KEULKS

Department of Chemistry and Laboratory for Surface Studies,
University of Wisconsin—Milwaukee, Milwaukee, Wisconsin 53201

AND

A. SKLIAROV, YU. MAXIMOV, L. YA. MARGOLIS AND O. V. KRYLOV

Institute of Chemical Physics, Academy of Sciences of the U.S.S.R.,
Moscow, U.S.S.R.

Received April 7, 1975

A number of spectroscopic techniques were used to obtain further information about the scheelite structure of compounds found in the ternary oxide system of bismuth, molybdenum, and iron. Infrared data indicated the presence of discrete tetrahedral and corner sharing octahedral molybdenum. Ultraviolet-visible spectroscopy provided evidence for the presence of an additional electronic level in the lattice, resulting in a shift of the charge transfer energy to longer wavelengths. The combination of ir and uv-visible spectroscopy indicated that at high temperatures distortion of the metal-oxygen bonds occurs. Iron was found to be present as Fe^{3+} and in two nonequivalent environments by Mössbauer spectroscopy. ESCA revealed that the surface layers contained bismuth, iron, molybdenum, and oxygen. ESCA measurements also revealed that Bi, Mo, and Fe were present in the surface layers as Bi^{3+}, Mo^{6+}, and Fe^{3+}, respectively.

INTRODUCTION

A number of investigations (*1–4*) have been concerned with the physicochemical and structural properties of the bismuth molybdate system which exhibits high activity and selectivity for the partial oxidation of olefins. Only a few such investigations of catalysts containing bismuth, iron, and molybdenum have appeared in the literature despite their high activity as described in several patients (*5–7*).

Daniel and Keulks (*8*) reported that the bismuth, iron, molybdenum system exhibited activity and selectivity comparable to bismuth molybdate and suggested the formation of a ternary compound which possibly was responsible for the catalytic activity and selectivity. The addition of iron to bismuth molybdate, investigated by Annenkova and co-workers (*9*), was found to increase the electrical conductivity and the activity for the oxidation of 1-butene. Batist and co-workers (*10*) investigated this system in the compositional range between α-bismuth molybdate and $Fe_2(MoO_4)_3$ and reported the existence of a new compound. Although this new compound was present in their catalysts along with considerable concentrations of bismuth molybdate and iron molybdate, they were able to conclude that this compound exceeded the α-phase of bismuth molybdate in activity to a considerable degree and maintained high selectivity. They suggested that this compound was responsible for the increased tendency of these catalysts to dissociate O_2 and possibly for the increased number of active sites.

---

[1] Work done at the Institute of Chemical Physics, Moscow, U.S.S.R.

[2] Exchange Fellow, U.S.A.–U.S.S.R. Cooperative Program in Chemical Catalysis.

Recently, an X-ray investigation by Lo Jacono and co-workers (*11*) revealed the presence of two ternary compounds in the bismuth iron molybdate system, with atomic ratio Bi/Fe/Mo = 1 : 1 : 1. The crystallographic structure of the first compound, which formed after calcination at 450°C, is tetragonal [space group C_{4H}^{6}–$I_{41/A}$ (88)] with parameters $a = 5.26$ Å and $c = 11.70$ Å. The second compound, which formed after calcination above 550°C, is monoclinic [space group $I_{2/A}$ (15)] with parameters $a = 5.40$ Å, $b = 11.70$ Å, $c = 5.24$ Å, and $\beta = 91°$. Another ternary compound within this system was observed with atomic ratio Bi/Fe/Mo = 3 : 1 : 2. The X-ray study of this system indicated that it exhibited the same crystallographic structure as that of the system Bi/Fe/Mo, 1 : 1 : 1.

Because certain conclusions were made about the structures of the bismuth iron molybdate system in the previous work (*11*) and because there is considerable interest in this system, we decided to study further the structure, valence states, and coordination of the various ions in this system by means of spectroscopic methods (ir, uv-VIS, ESCA, and Mössbauer).

EXPERIMENTAL METHODS

The surface area of the catalysts was measured by the chromatographic thermodesorption of argon (see Table 1).

The infrared spectra were obtained by the KBr disk method with a Carl-Zeiss spectrometer UR-20 (DDR) in the range 400 cm^{-1} to 20,000 cm^{-1}, using a concentration of 2 mg/cm^2. The spectra are presented in Fig. 1, where transmittance has been plotted versus the wavenumber. The spectra of well-characterized α- and γ-bismuth molybdates, presented for comparison, are in agreement with those previously published (*12*). The α-bismuth molybdate shows the characteristic bands at 955, 940, 910, 870, 850, and 840 cm^{-1} which are associated with the ν_1 and ν_3 group vibrations of the edge sharing distorted $Mo_2O_8^{4-}$ tetrahedra groups present in this phase. The γ-bismuth molybdate shows the characteristic bands at 850, 805, 750, and 560 cm^{-1} associated with the group vibrations of corner sharing MoO_6 octahedra. The spectrum of sample 12a shows bands at 930, 845, 810, 740, and a broad band at 550 cm^{-1}. In contrast to sample 12a, the spectrum of sample 12b shows a well-stabilized structure with characteristic bands at 965, 880, 845, 815, 750, 575, and 540 cm^{-1}. The spectrum of sample 14a, in the system Bi/Fe/Mo = 3 : 1 : 2, shows broad bands at 880, 810 750, and 545 cm^{-1}, while sample 14b shows more sharp bands at 880, 845, 815, 745, 575 (shoulder), and 545 cm^{-1}.

The uv-VIS spectra were obtained with a Specord uv-VIS (DDR) and are presented in Fig. 2. The spectra show the start of intensive absorption from 16,000 to 20,000 cm^{-1}. The spectrum of α-bismuth molybdate with tetrahedral molybdenum agrees with that previously published (*10*) and shows the start of charge transfer at 23,400 cm^{-1}. The γ-bismuth molybdate with octahedral molybdenum shows the start of charge transfer at 21,000 cm^{-1}. Catalysts 12a and 12b show that the charge transfer (16,670 and 16,400 cm^{-1}, respectively) is shifted considerably to the long wavelength side of the spectrum. In the case of catalysts 14a and 14b, it is possible to see charge transfer at 18,150 and

TABLE 1

Composition and Surface Area of the Bi–Fe–Mo System

Atomic ratio Bi/Fe/Mo	Calcination temp (°C)	Specific area (m^2/g)	Index of samples
1 : 1 : 1	450	5.2	12a
	600	3.5	12b
3 : 1 : 2	450	1.5	14a
	600	1.0	14b

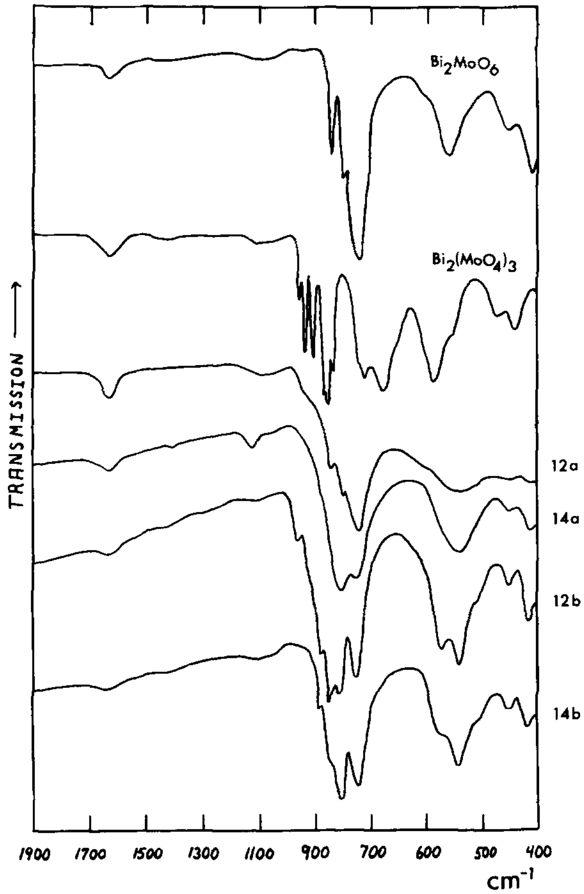

FIG. 1. Infrared spectra.

19,700 cm^{-1}, respectively. Broad *d–d* transition bands with low intensity were also observed at 15,000 cm^{-1} (for samples 12b and 14b) and at 19,000 cm^{-1} (for sample 14b). The *d–d* transition at 15,000 cm^{-1} has been connected with Mo(V) (*13*) while the *d–d* transition at 19,000 cm^{-1} is possibly connected with Fe(III) because bands in this region have previously been associated with iron (*14*).

ESCA measurements were made with an AEI, Model ES-100, spectrometer on catalysts 12b and 14b at room temperature. The Al K_α line (1487 eV) was used for excitation, and the peaks were referenced to the C-1*s* peak resulting from oil contamination in the vacuum system. The X-ray generator was operated at 15 kV and 15 mA. The samples were mounted on fine brass-wire grids to minimize sample reduction. The spectra for catalysts 12b and 14b are presented in Fig. 3.

The Mössbauer spectra of samples 12b and 14b were obtained at 80 and 300°K with an electrical dynamic type apparatus equipped with a ^{57}Co in Cr source. The isomer shifts were measured from the center of the hyperfine structure of α-Fe. The spectrum of sample 12B at 80°K, Fig. 4a, showed the superposition of two nonequivalent spectra. The sextet, having the hyperfine structure with effective magnetic field $H_{\text{eff}} \approx 540 \pm 5$ kOe results from Fe^{3+} with magnetic ordering in certain regions of the crystal. The H_{eff} has parameters

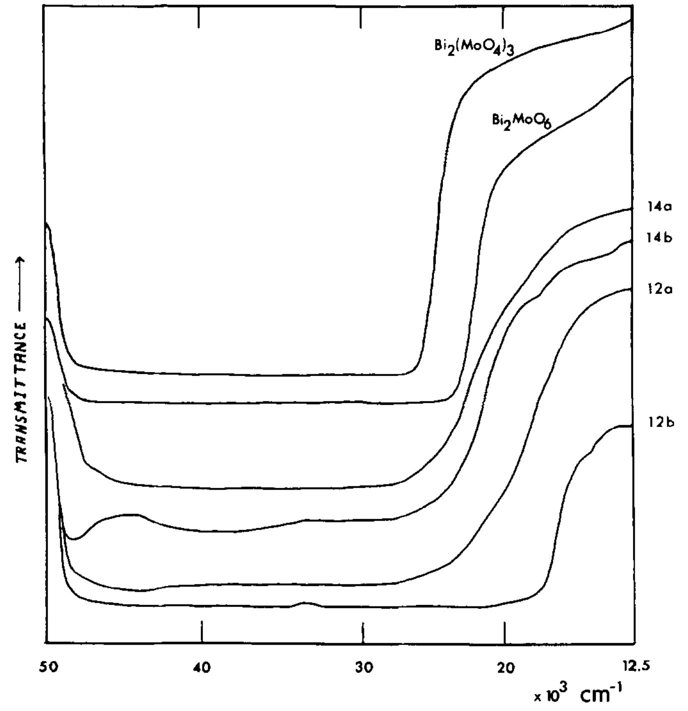

FIG. 2. Ultraviolet-visible spectra.

similar to those of antiferromagnetic α-Fe_2O_3, however, α-Fe_2O_3 was not observed in the X-ray pattern or in the infrared spectra. In addition to the sextet, an asymmetric doublet with isomer shift ($\delta E_I = 0.35 \pm 0.07$ mm/sec) and quadrupole splitting ($\Delta E_Q = 1.00 \pm 0.07$ mm/sec) was located in the center of the spectrum and results from paramagnetic iron Fe^{3+} in a crystalline field of axial symmetry. The amount of paramagnetic iron relative to the amount of magnetically ordered iron is 3/1, assuming equal values of f'.

A change in the magnetic ordering was observed for this sample at 300°K (Fig. 4b). The lines of the hyperfine structure have broadened, probably a splitting occurs, and indicate two systems of iron with magnetic ordering, each having a characteristic hyperfine structure. These two systems may result from the interaction of iron in two nonequivalent positions in the lattice. Since the value of ΔE_Q for the doublet remains nearly constant, the most important factor on the quadrupole interactions is the influence of the crystalline field.

A doublet which indicates Fe^{3+} in a very distorted crystal field is observed in the spectrum of sample 14b at 80°K (Fig. 3c). The parameters of this doublet are approximately the same as the parameters of the doublet of sample 12b. The asymmetry is apparently caused by the Goldansky–Koryagin effect (*17*) for polycrystalline samples. The spectrum of sample 14b at 300 °K was nearly the same as the spectrum at 80°K and is, therefore, not presented.

These spectra indicate that the iron present in both catalysts 12b and 14b is Fe^{3+}. The iron in sample 14b has an extremely distorted environment. In contrast to sample 14b, in sample 12b approximately one-half of the iron ions participate in antiferromagnetic exchange interaction which occurs by Fe–O–Fe interactions in the lattice. The comparison of spectra for

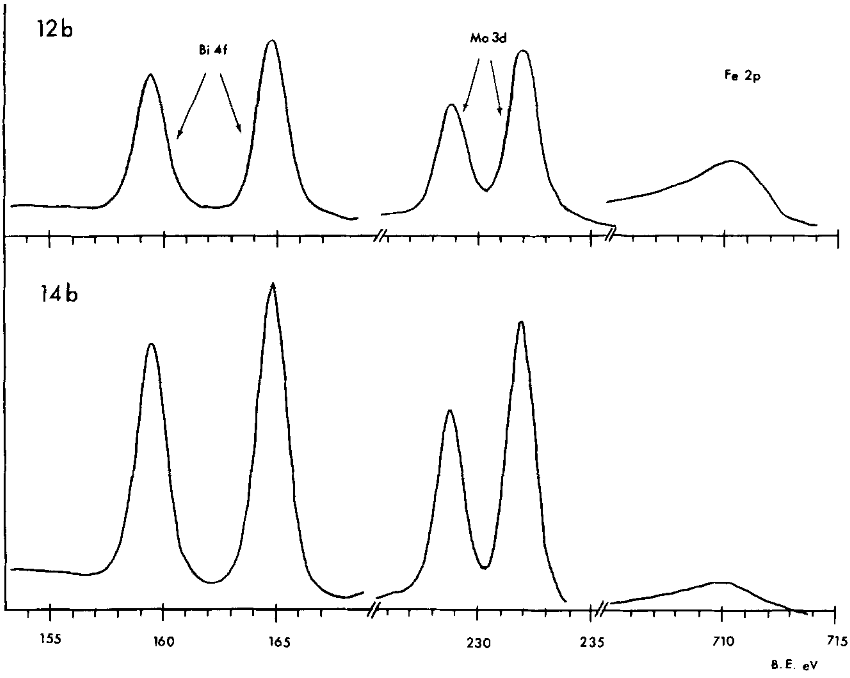

FIG. 3. ESCA Spectra for samples 12b and 14b.

sample 12b at 80 and 300°K revealed that for both magnetic sublattices different magnetic stability exists in contrast to α-Fe_2O_3, resulting from the different quantity of magnetic and nonmagnetic ions present in these magnetic sublattices. These results show that in the crystal some regions exist with increased local concentration of iron (magnetic clusters). Iron, which is surrounded by nonmagnetic molybdenum as its nearest neighbors, results in the doublet of paramagnetic iron.

Differential thermal and thermogravimetric analysis of the samples 12 and 14 were carried out with a Paulic Paulic pyrometer equipped with a programming device to provide a uniform rise in temperature at a predetermined rate. The samples were placed in platinum crucibles, and the temperature was measured with platinum–platinum rhodium thermocouples with a simultaneous measure of the weight of the sample.

Samples 12 and 14 showed an exothermic peak at 300 and 250°C, respectively, corresponding to the formation of compounds 12a and 14a. Compound 12a is well-formed at 380°C and is stable until 540°C, at which temperature an endothermic peak appears together with an increase in weight of the sample. This indicates that compound 12b is formed at 540°C, and its formation is probably accompanied by the absorption of oxygen. The compound 12b is stable until its melting point at 912°C. The data indicate that compound 14a is well-formed at 350°C and is stable until 480°C at which temperature there is an endothermic peak and an increase in weight corresponding to the formation of 14b. Compound 14b is stable until its melting point at 908°C. The presence of additional oxides or binary compounds was not observed in the analysis of these two ternary compounds. The close relationship of catalysts 12 and 14 is reflected in the similar thermal and gravimetric behavior in the formation of these

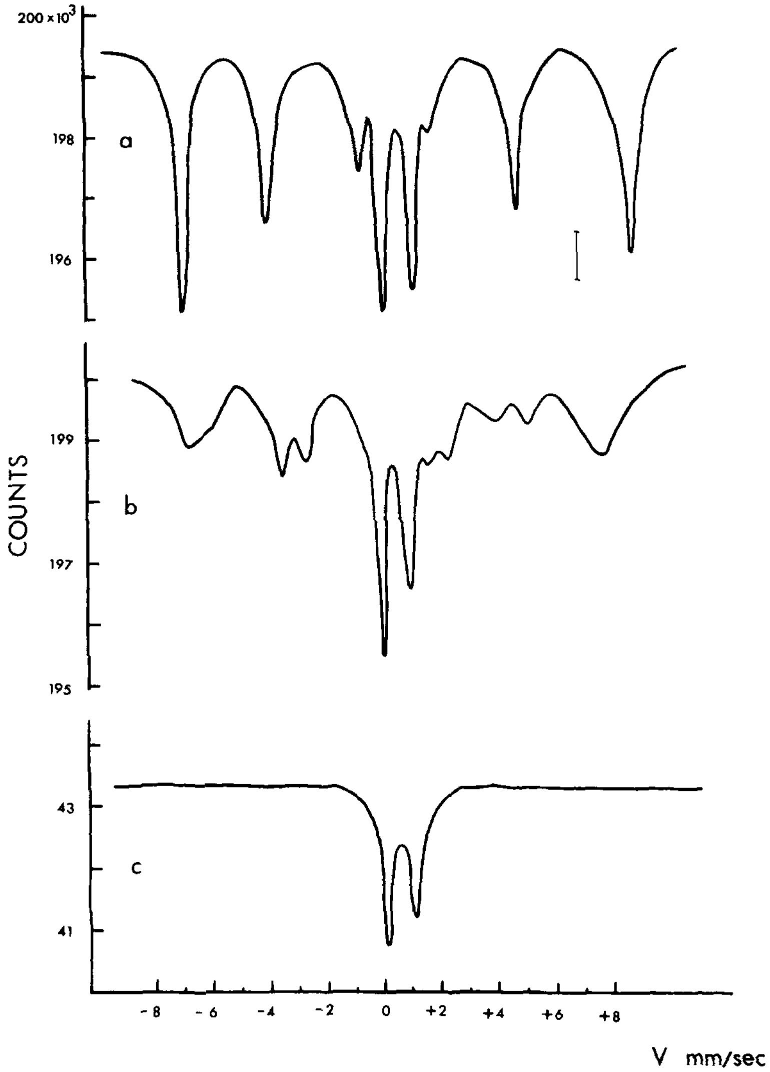

FIG. 4. Mössbauer spectra. (a) Spectrum of sample 12b at 80°K; (b) spectrum of sample 12b at 300°K; (c) spectrum of sample 14b at 80°K.

compounds as well as the close melting points.

DISCUSSION

On the basis of an X-ray investigation, the authors (*11*) explained the composition and close structural relationship of the bismuth iron molybdate compounds with the scheelite related $Bi_2(MoO_4)_3$ structure (with ordered vacancies) by proposing in the case of Bi/Fe/Mo = 1 : 1 : 1 that one Mo^{6+} ion is replaced by two Fe^{3+} ions; one Fe^{3+} ion (ionic radius 0.64 Å) replaces Mo^{6+} (ionic radius = 0.62 Å); the other Fe^{3+} ion occupies one of the vacancies. In the compound Bi/Fe/Mo = 3 : 1 : 2, the Fe^{3+} ion replaces one Mo^{6+} ion while the additional Bi^{3+} ion occupies one of the vacancies. This type of substitution would account for the stabilization of the scheelite structure.

In this study, infrared spectroscopy was used to investigate the detailed structure of these catalysts. The spectrum of sample 12a has absorption bands at 845 and 740 cm^{-1} which are characteristic of the group vibrations of corner sharing MoO_6 octahedra (*15*). The spectrum of catalyst 12b indicates a change in coordination has occurred at the higher calcination temperature. The sharp absorption band at 815 cm^{-1} is associated with the ν_3 group vibrations of discrete tetrahedra in this compound (*16*). In addition to the tetrahedra, the group vibrations of corner sharing MoO_6 octahedra are also present although the appearance of the bands at 880 and 970 cm^{-1} indicate a distortion of the octahedra possibly caused by bridging. The slight shoulder at 800 cm^{-1} probably indicates the presence of traces of iron molybdate as detected by XRD (*11*).

Unlike catalyst 12a, the group vibrations of the discrete tetrahedra are present in the catalyst 14a together with the group vibrations of corner sharing octahedral MoO_6. The spectrum of catalyst 14b is similar to the spectrum of 14a except for an increase in sharpness of the bands, and the octahedral molybdenum are again seen to become distorted due to bridging at the higher temperature.

A comparison of the ir spectra of the ternary compounds with the spectra of oxides and binary compounds of bismuth, iron, and molybdenum (9) revealed the absence of oxides and binary compounds with the exception of traces of iron molybdate present in 12b. The spectra of 12b and 14b calcined at 750°C for 20 hr revealed the stability of these ternary compounds at high temperatures.

Analysis of the spectra of the bismuth iron molybdate system shows that the ir spectra of the catalysts differ from the spectra of α- and γ-bismuth molybdate. This indicates that the effect of iron addition to the bismuth molybdate system causes a change in coordination. Noticing the close structural relationship of these catalysts with the α-bismuth molybdate, the same effect which accounted for the stabilization of the scheelite structure can also account for the change in coordination, i.e., the proposed presence of Fe^{3+} in the Mo^{6+} position accounted for the stabilization of the scheelite structure and the presence of Fe^{3+} in a Mo^{6+} position also accounts for the discrete tetrahedra. The presence of iron in the molybdenum position would result in the distortion of the tetrahedra groups and a shift in the absorption band from that characteristic of tetrahedral groups to a band at lower energies characteristic of discrete tetrahedra.

The spectra also show corner sharing octahedral molybdenum. Their formation can possibly be associated with oxygen bond rearrangements brought about by Fe occupying the vacancy position, i.e., Mo_2O_8 edge sharing tetrahedral group→ Mo_2O_8 corner sharing octahdral group.

The presence of two nonequivalent magnetic states of Fe^{3+}, indicated by Mössbauer measurements for catalyst 12b, can be explained by iron occupying two different positions in the structure, i.e., iron occupying the ordered vacancies and the paramagnetic iron occupying one of the Mo positions in the α-bismuth molybdate structure. This explanation is further supported by the presence of only one type of iron in sample 14b where, in order to account for the crystallographic structure, the Fe ion was proposed to occupy a Mo position.

The analysis of the uv-VIS spectra shows the charge transfer energy is shifted to the long wavelength side of the spectrum. The addition of iron to the bismuth molybdate system results in the formation of an additional electronic level and a consequent shift to the long wavelength side of the spectrum. This shift is seen to be pronounced in catalysts 12a and 12b where the concentration of iron is greater than in catalysts 14a and 14b. An additional effect observed is the increase in charge transfer energy with greater distortion. The compounds formed at higher calcination temperature 12b and 14b are seen to have the charge transfer energy shifted to the short wavelength side compared to catalysts 12a and 14a, respectively. The increased distortion at higher temperatures was seen by ir.

The ESCA results indicate that all three elements, Bi, Mo, and Fe, are present in the surface layers. From a comparison of published values for binding energies (*18,19*) we conclude that Bi is present as Bi^{3+}, Mo as Mo^{6+}, and Fe as Fe^{3+}. This observation is in contrast to Wolfs (*19*), who detected only Bi and Mo in the surface layers of multicomponent catalysts containing Bi, Mo, and Fe, but is consistent with our contention that catalysts 12b and 14b are indeed ternary compounds.

In summary, the results obtained in this investigation are consistent with and support the previous proposal of the formation of ternary compounds when iron is introduced into the bismuth molybdate system. These structures exhibit distorted coordination, i.e., bond energy and bond lengths of the metal–oxygen bonds are changed. The coordination of molybdenum, charge transfer energy, and additional presence of iron in scheelite-type structures of these compounds present an interesting comparison with the various bismuth molybdate phases.

ACKNOWLEDGMENTS

The authors express appreciation to Dr. I. P. Suzdalev, O. S. Morosova, K. N. Spiridonov, and G. V. Antoshin for useful discussions and assistance. The authors also gratefully acknowledge partial financial support for this work from the National Science Foundation, U.S.A., and from the Academy of Sciences, U.S.S.R.

REFERENCES

1. Margolis, L. Y., *Catal. Rev.* **8,** 241 (1973).
2. Erman, L. Y., Gol'perin, E. L., Kolchin, I. K., Dobrzhanskii, G. F., and Chernyshev, K. S., *Russ. J. Inorg. Chem.* **9,** 1174 (1964).
3. Batist, P. A., Bouwens, J. F. H., and Schuit, G. C. A., *J. Catal.* **25,** 1 (1972).
4. Van den Elzen, A. F., and Rieck, G. D., *Acta Crystallogr., Sect. B* **29,** 2433 (1973).

U.S. Pat. 3,110,746, 1964.

6. *U.S. Pat.* 3,454,630, 1969.
7. *Netherlands Pat.* 7,006,454, 1970.
8. Daniel, C., and Keulks, G. W., *J. Catal.* **29,** 475 (1973).
9. Annenkova, I. B., Alkhazov, T. G., and Belen'kii, M. S., *Kinet. Katal.* **10,** 1305 (1969).
10. Batist, P. A., Van de Moesdijk, C. G. M., Matsuura, I., and Schuit, G. C. A., *J. Catal.* **20,** 40 (1971).
11. Lo Jacono, M., Notermann, T., and Keulks, G. W., unpublished data.
12. Trifiro, F., Hoser, H., and Scarle, R. O., *J. Catal.* **25,** 12 (1972).
13. Mitchell, P. C. H., *Quart. Rev. Chem. Soc.* **20,** 103 (1966).
14. Wolfs, M. W., and Batist, P. A., *J. Catal.* **32,** 25 (1974).
15. Mitchell, P. C. H., and Trifiro, F., *J. Chem. Soc., A* 3183 (1970).
16. Nakamato, K., "Infrared Spectra of Inorganic and Coordination Compounds." Wiley, New York, 1964.
17. Goldansky, V. I., and Makarov, E. F., "The Chemical Applications of Mössbauer Spectroscopy." (in Russian), Mir Publ., Moscow, 1970.
18. Baker, A. D., and Betteridge, D., "*Photoelectron Spectroscopy.*" Pergamon, Elmsford, NY, 1972.
19. Wolfs, M. W., thesis, Technische Hogeschool, Eindhoven, The Netherlands, 1974.